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Ab initio Calculations of the Chiroptical Properties of Z-Configured Polymethine Dyes

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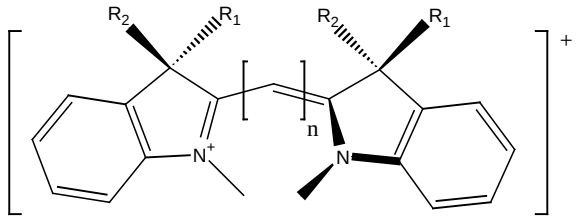
Ab initio calculations of a series of inherently chiral, all-Z-configured polymethine dyes



n=1: monomethine, **1**
n=3: trimethine, **2**
n=5: pentamethine, **3**

n = 1, 3, 5, 7, ...

are presented. The experimentally known chiroptical properties of the monomethine **1** and trimethine **2** make these compounds and their homologue **3** ideally suited to test the applicability of quantum mechanical calculations.

In compound **1** the chromophore is forced into a twisted all-Z-conformation by steric interaction of the end groups, while in **2** the presence of a t-butyl group in the *meso*-position enforces this conformation, which is manifest in the UV/Vis spectra not only in the reduced intensity of the longest wavelength absorbtion (methine band), but also in the occurrence of a „cis-peak“ at shorter wavelengths[1].

Using the *MOLCAS* program-package excited states were calculated with the *CASSCF* and *CASPT*2 methods. Electric and magnetic dipole transition moments were calculated, yielding UV/Vis and CD-spectra in good agreement with experimental results. The negative sign of the CD-band observed for P-helical monomethine **1** which appears to violate established helicity rules can be understood with the aid of a component analysis[2,3] and was confirmed by the quantitative calculations. Additional calculations on the as yet not synthesized pentamethine **3** allow to predict the theoretical spectra of this compound.

[1] L. Zechmeister, Chem. Rev. 34 (**1944**) 267
[2] L. Eggers, V. Buß, G. Henkel, Angew. Chem. 108 (**1996**) 973
[3] L. Eggers, K. Kolster, V. Buß, Chirality 9 (**1997**) 243